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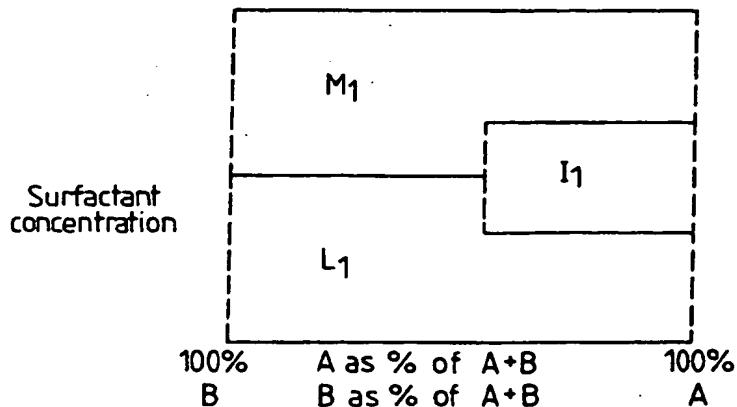
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(54) Novel cleaning compositions.

(57) Aqueous based VI phases (ringing gels) are used as laundry pre-spotters, e.g. in stick applicators, and for a variety of cleaning applications. The compositions typically comprise a non-ionic surfactant having an HLB greater than 15, a surfactant having an HLB below 10 and water.

Fig. 3



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The present invention relates to novel cleaning compositions which are high viscosity gels at ambient temperature, but which are preferably liquefiable or dispersible at laundry washing temperature. In particular it provides compositions which can be obtained in the form of dimensionally stable sticks or bars, suitable for application to surfaces by friction.

5 The process of washing clothes (or laundry) in an automatic washing machine comprises a timed washing cycle, followed by a set number of rinses. The timed wash is herein referred to as the mainwash cycle and under normal washing conditions is relied upon to remove all soils and stains from the laundry. However, with articles that are heavily soiled (for example with body fats) or heavily stained (for example with blood) the mainwash cycle alone may not be sufficient to provide a satisfactory result with regard to  
10 the cleanliness of the laundered clothes.

To facilitate the cleaning of heavily soiled clothes or the removal of stubborn stains, a pre-wash cycle of shorter duration than the subsequent mainwash cycle is available on automatic washing machines, and is used in addition to the latter if required.

Although a pre-wash cycle is effective in providing a cleaner washing result when used in conjunction  
15 with the mainwash cycle, than the latter alone, it is inefficient to treat the entire washing load if only a small proportion of the load requires this additional treatment.

With energy and chemical wastage undesirable on environmental and economic grounds, there is an increasing tendency to avoid pre-washing, and instead to treat laundry which requires additional cleaning to  
20 that provided by the mainwash, with a 'pre-spotting' detergent composition. By use of the aforementioned composition, detergents are applied only, and directly, to soils and stains present on the laundry. Obviously this reduces energy wastage when compared to pre-washing as an additional washing machine cycle is now not required, the pre-spotting detergent being removed from the fabric during the mainwash machine cycle. By applying the detergent composition directly and specifically to the area requiring treatment the quantity of detergent required is reduced for pre-spotting in comparison to pre-washing. One possible  
25 method of applying detergent to a limited area is a stick applicator.

Stick applicators are well known. They comprise a container, one end of which is open or capable of being opened and a solid, plastic or gel composition at least predominantly within the container, but capable of being progressively exposed at the open end, and adapted to be applied to a surface by friction between the surface and the exposed part of the composition. Typical examples of stick applicators include  
30 lipstick, shaving soap, pencils, deodorant sticks and laundry pre-spotting or stain removal sticks.

In a typical stick applicator the container, usually having a substantially constant cross section at all points along its axis, is open at one end, and is typically provided with removable closure means. The applicator may be provided with means for extruding the contents progressively through the open end. For example the extrusion means may comprise a screw extruder, e.g. one in which the rotation of a base  
35 member causes a plunger to move along the axis of the container. Alternatively the plunger may be actuated by sliding means such as nested concentric tubes telescoped by pressure between the top and base or lugs projecting laterally through slots in the container.

An alternative to extrusion means is a container whose sides are adapted to be progressively removed to expose the contents as the latter is consumed. For example the side of the container may comprise a foil  
40 which can be peeled back or may be in the form of a wooden tube which can be cut back with a knife or pencil sharpener.

The term "stick applicator" will be used herein to include all the aforesaid types of applicator.

Currently commercially available 'pre-spotting' detergent compositions used in stick applicators are usually of a 'soap-bar' type, which have the disadvantages of not being able readily to accommodate  
45 enzymes, which help to remove soils and stains commonly encountered in laundry, and of requiring wetting with water followed by vigorous rubbing over the treatment area. Currently available liquid laundry detergents have been recommended as pre-spotting agents. They are directly applied by pouring onto the soiled/stained fabric followed by gentle rubbing to aid the penetration of the detergent into the fabric. However, this method of application is not guaranteed to treat the specific area requiring attention, and  
50 moreover uses more product than is necessary. The manual 'rubbing in' of the product is also undesirable and there is a risk of spillage and a tendency to be messy.

One object of our invention is to provide a cleaning composition suitable for use as a pre-spotter which overcomes the above problems of existing prespotters and which is easy to apply to stains and effective at reducing or removing them.

55 For the removal of soil or stains from soft furnishings such as carpets, curtains or upholstery the treatment of the whole object to remove a small area of soil or stain is uneconomical. Furthermore, overwetting of upholstery or carpet is undesirable as shrinkage may occur, or there may be problems in ensuring the wetted article becomes completely dry, for example the interior of settees. Conventional

upholstery cleaners are usually liquid formulations designed to be applied as a dilute solution, manually rubbed over the area requiring treatment and left to dry. This obviously involves an undesirable volume of water which in turn necessitates a prolonged drying time. Spray-on formulations are also available, which dry to a foam and require brushing or vacuuming of the treated area to remove the foam and soil.

- 5 A second object of our invention is to provide a cleaning composition suitable for use in removing soils and stains from areas of soft furnishings, which does not require large amounts of water, brushing or vacuuming of the fabric or fibres.

Another consideration for the detergent industry in order to reduce packaging, transport and storage costs and increase efficient use of retail shelf space, is to formulate products at higher payloads than have 10 hitherto been commercially available.

An advantage of both compact laundry powders and concentrated liquid laundry detergents is that they contain higher payloads than do traditional laundry products, thus requiring smaller dosages per wash when using a concentrated product. For the consumer, this feature reduces the bulk of the product to be carried home, and the market requirement is for even more concentrated laundry products to maximise this benefit 15 to the consumer.

However, the concentrated powder and concentrated liquid laundry compositions are often unacceptable to the consumer. The former have a tendency to be sticky, and thus cake on storage, whilst the latter are usually anhydrous formulations which do not exhibit good rinseability in the wash, often leaving a gel residue in the liquid dispenser. Furthermore, the formation of this gel, which is difficult to disperse, lowers 20 the surfactant concentration in the wash liquor and is therefore detrimental to the washing performance of the anhydrous liquid product.

Compact and traditional laundry powders are packaged in boxes, with any hole, tear or improperly sealed edge allowing the spillage and loss of powder. Furthermore, if the packaging boxes become damp during storage the powder detergent becomes moist, cakes inside the box and so will not dispense easily.

25 Concentrated and standard laundry liquids will spill if the container bursts, or is accidentally knocked over, whilst the viscosity and flow characteristics of the laundry liquid renders it potentially messy.

With both powder and liquid formulations there is a temptation and tendency for the consumer to overdose with product, this encourages wastage and to some extent negates the advantages obtained by increasing the payload of the product.

30 A third object of this invention is therefore to provide an aqueous based detergent composition which may be supplied in pre-dosed portions and in a physical form which is less likely to lead to spillage of the product, and contains a high payload.

Another type of cleaning product which is often inconvenient to use in practice is the hard surface cleaner. A typical hard surface cleaner comprises a cream or paste containing surfactants and inert abrasive 35 particles. Creams may typically be poured directly on to stained horizontal surfaces such as hobs and kitchen work tops and wiped or rinsed off with a wet cloth. Cleaning vertical surfaces such as walls, doors or windows requires the compositions to be applied first to the cloth. Both these methods of application tend to be wasteful of the product and are messy and inconvenient, with potential for spillage.

A fourth object of our invention is therefore to provide a hard surface cleaner in a form which is more 40 convenient to use than the known products.

Similarly to hard surface cleaners, products for cleaning human skin such as toilet soap and heavy duty hand cleaning gels are usually uneconomical and messy to use. For example gels of high surfactant concentration, commonly used in situations such as in factories or garages where the nature of people's work requires a heavier duty product, are customarily soft, solvent-based gels which are packaged in tubs. 45 This type of packaging encourages the user to cover his hands entirely in such a hand cleaning formulation, which only produces the desired cleansing effect, at the cost of uneconomical usage of the product. Usually such products are solvent-based and may with repeated washing have a drying or defatting effect upon the skin. Solvent based products are also undesirable on environmental grounds. Toilet soaps tend to become slimy after use due to formation of curdy gels on the wetted surface. Such gels also tend to accumulate in 50 soap dishes.

Petcare formulations for the cleansing of animal skin and fur, for example dog and cat shampoos, are customarily liquid products which are messy to use and uneconomical with the potential for spillage.

A fifth object of the invention is therefore to provide an aqueous based detergent composition for use as a skin cleanser which is in a more convenient to use form than known products, and which has the 55 advantage of not requiring solvents. Other toiletry products which may be formulated to provide an easier to use form of product than those currently available include shaving sticks, shower gels and shampoos. Petcare shampoo formulations may be provided as aqueous based detergent compositions which are in an easier to use form than conventional petcare shampoos. Such petcare shampoos formulations may contain

conventional amounts of minor ingredients such as biocides, insecticides and conditioning agents.

A particular disadvantage of liquid laundry detergents is the difficulty of incorporating enzymes, which tend to be unstable in liquid detergents. This is particularly true of mixed enzyme systems containing protease and lipase. Ideally an enzyme system should include protease, amylase and lipase. This is the preferred combination used in detergent powders. The enzymes protease and lipase are incorporated into laundry detergent formulations for their ability to remove proteinaceous stains (e.g. blood and milk) and fatty stains (e.g. sebum) respectively. However, when protease and lipase are present together in a laundry liquid composition, the product medium allows interaction of the two aforementioned enzymes, with rapid deterioration of lipase activity resulting as lipase is destroyed by the presence of protease. Although enzymes are included in powder detergents, they would give rise to problems of allergenic dust, and also loss of activity, on spray drying, and therefore have to be post added which causes serious problems in manufacture. They also tend to be inactivated by bleach in the powder.

A sixth object of the invention is therefore to provide an aqueous based detergent composition, containing a stable enzyme system and especially one which includes both a lipase and a protease.

A further problem which is encountered with known aqueous based detergents is the difficulty of incorporating oxidising bleaches such as perborates, percarbonates, peroxides or hypochlorites.

Such oxidising bleaches have the ability to improve the stain removal performance of a laundry product. Tannin from tea, and red wine are two examples of bleachable stains commonly encountered in a washing load. The inherent water-sensitivity of the aforementioned bleaches has hitherto made inclusion into aqueous based laundry products difficult, resulting in a loss of activity of the bleach, and ultimately its decomposition.

Alternative concentrated solvent based (non-aqueous) laundry products have been developed to comprise bleach, although the high levels of solvents present in such formulations are undesirable on environmental grounds.

A seventh object of this invention is therefore to provide an aqueous based laundry detergent containing an oxidising bleach.

Detergent powder has, for many years, been manufactured by making a slurry in water of the surfactant, builder and filler together with various ancillary ingredients, and spray drying or fluid bed drying the slurry to form a powder. The heat and aggressive environment of a spray dry slurry prevent sensitive ingredients such as enzymes and bleaches being added at that stage.

Numerous attempts have been made to overcome the problems of incorporating sensitive ingredients, by encapsulation and/or by dry blending them into the powder after spray drying. These attempts have not provided an acceptable solution to the problem. Dry blending gives a risk of inhomogeneity which would be a serious health and safety hazard to the consumer, and requires the handling of allergenic or corrosive powders which cause hazards to the manufacturer. Encapsulation has failed to provide adequate protection for bleaches, which have not been successfully incorporated into a commercially viable liquid formulation.

The cost of spray drying and the cost of the filler, which does not fulfil any useful function in the wash and may even have a negative effect contribute significantly to the cost of detergent powder. The filler also contributes substantially to the bulk of a conventional laundry powder, which is convenient for shoppers to carry and store and undesirable for the retailer because it takes up valuable shelf space.

A further object of this invention is therefore to provide particulate or granular detergent compositions which do not require spray drying and into which sensitive ingredients can be incorporated without dry blending.

Another problem concerns softeners and other fabric conditioners. The most effective of these are cationic materials, typically having two long chain alkyl (especially tallowyl) groups, e.g. dimethyl ditallowyl ammonium chloride. Because of their cationic character they cannot be incorporated in conventional anionic laundry detergents without impairing the washing effectiveness of the product. They have to be post-added at the rinse stage, necessitating the use of a separate product.

A further object of this invention is to provide a means of encapsulating bleaches, such as sodium perborate, or any other water or detergent sensitive materials with an aqueous based surfactant composition. This permits otherwise incompatible materials to be incorporated into liquid or powder detergents with reduced tendency to inactivation.

Surfactants are known to form mesophases or liquid crystal phases at concentrations above approximately 30% by weight based on the weight of water and surfactant. Mesophases are phases which exhibit a degree of order intermediate between typical liquids and solids. Generally mesophases combine long range order associated with crystals, with fast molecular motion common to liquids.

The formation of detergent mesophases is well documented. Different surfactants and surfactant mixtures differ widely in their ability to form the numerous different mesophases, and in respect of the

conditions of concentration and temperature at which they are formed. For a typical surfactant of the type normally used in cleaning products the following mesophase are usually observed. The concentrations given are illustrative only and may vary considerably from one surfactant or surfactant mixture to the next.

Below approximately 30% surfactant an isotropic L<sub>1</sub> phase is formed (with micelles of surfactant in water). Above 30% surfactant many detergents form an M phase which is of no value in laundry applications since it does not show suitable flow characteristics and is difficult to dissolve or disperse in water. Above the concentrations required to form an M-phase, but usually at concentrations of less than 80% active surfactant i.e. 60%-80% a G-phase is formed. At concentrations higher than those required to form a G-phase i.e. typically greater than 80% active surfactant, most surfactants form a hydrated solid, and some, especially non-ionic surfactants form a liquid phase containing dispersed micelle sized droplets of water-an inverted micellar solution known as an L<sub>2</sub> phase. Although such a surfactant system would appear ideal for use as a laundry detergent, L<sub>2</sub> detergent systems do not disperse readily in water and have a tendency to form undesirable gels, e.g. M phases, on dilution.

Some surfactants form viscous isotropic or VI phases. These are immobile phases usually with a vitreous appearance, and have been relatively little studied compared to the other phases discussed above. They have been virtually ignored in the context of formulating cleaning compositions because most of the surfactants and surfactant systems which are commonly used in cleaning compositions do not form VI phases, at least at normal temperatures, or form them only within narrow concentration ranges and because their known properties as immobile gels has deterred formulators from investigating them. They are recognised as being the most viscous of the lyotropic mesophases. Conventional wisdom has dictated that a commercially acceptable cleaning composition, particularly in the laundry and hard surface cleaning areas must be either a free flowing powder or a mobile liquid.

The different surfactant phases can be recognised by a combination of appearance, rheology, textures under the microscope, electron microscopy and x-ray diffraction or neutron scattering. A detailed description, with illustrations, of the different textures observable using a polarising microscope, is to be found in the paper by Rosevear JAOCs Vol 31, p628.

The following terms may require explanation or definition:

The "hydrophilic: lipophilic balance", or "HLB" value is used as a measure of the relative affinities of surfactants for water and oil respectively and correlates with their effectiveness as emulsifiers. HLB value can easily be calculated for alcohol ethoxylates since it is one fifth of the weight percent of ethylene oxide based on the total mole weight. Other surfactants can be assigned equivalent values by applying more complicated formulae or by measuring their relative affinity for water and oil. An HLB value of 20 represents a completely water soluble oil insoluble surfactant, whilst an HLB value of 0 represents a completely oil soluble and water insoluble surfactant. For surfactant mixtures for use in laundry detergent products, an HLB value of 12 is commonly considered to provide the maximum washing efficiency, and thus laundry compositions are ideally formulated to incorporate surfactant systems with an HLB as close to 12 as possible.

"Optically isotropic" surfactant phases do not normally tend to rotate the plane of polarisation of plane polarised light. If a drop of sample is placed between two sheets of optically plane polarising material whose planes are at right angles, and light is shone on to one sheet, optically isotropic surfactant samples do not appear substantially brighter than their surroundings when viewed through the other sheet. Optically anisotropic materials appear substantially brighter. Optically anisotropic mesophases typically show characteristic textures when viewed through a microscope between crossed polarisers, whereas optically isotropic phases usually show a featureless continuum.

"Newtonian liquids" have a viscosity which remains constant at different shear rates. For the purpose of this specification, liquids are considered Newtonian if the viscosity does not vary substantially at shear rates up to 1000 sec<sup>-1</sup>.

"Lamellar" phases are phases which comprise a plurality of bilayers of surfactant arranged in parallel and separated by liquid medium. They include both solid phases and the typical form of the liquid crystal G-phase. G-phases are typically pourable, non-Newtonian, anisotropic products. They are typically viscous-looking, opalescent materials with a characteristic "smeary" appearance on flowing. They form characteristic textures under the polarising microscope and freeze fractured samples have a lamellar appearance under the electron microscope. X-ray diffraction or neutron scattering similarly reveal a lamellar structure, with a principal peak typically between 4 and 10nm, usually 5 to 6nm. Higher order peaks, when present occur at double or higher integral multiples of the Q value of the principal peak. Q is the momentum transfer vector and is related, in the case of lamellar phases, to the repeat spacing d by the equation

$$Q = \frac{2n[\rho_i]}{d}$$

5 where n is the order of the peak.

G-phases, however, can exist in several different forms, including domains of parallel sheets which constitute the bulk of the typical G-phases described above and spherulites formed from a number of concentric spheroidal shells, each of which is a bilayer of surfactant. In this specification the term "lamellar" 10 will be reserved for compositions which are at least partly of the former type. Opaque compositions at least predominantly of the latter type in which the continuous phase is a substantially isotropic solution containing dispersed spherulites are referred to herein as "spherulitic". Compositions in which the continuous phase comprises non-spherulitic bilayers usually contain some spherulites but are typically translucent, and are referred to herein as "G-phase compositions". G-phases are sometimes referred to in the literature as 15  $L_{(\alpha)}$ -phases.

$L_1$ -phases are mobile, optically isotropic, and typically Newtonian liquids which show no texture under the polarising microscope. Electron microscopy is capable of resolving the texture of such phases only at very high magnifications, and X-ray or neutron scattering normally gives only a single broad peak typical of a liquid structure, at very small angles close to the reference beam. The viscosity of an  $L_1$ -phase is usually 20 low, but may rise significantly as the concentration approaches the upper phase boundary.

"M-phases" are typically immobile, anisotropic products resembling low melting point waxes. They give characteristic textures under the polarising microscope, and a hexagonal diffraction pattern by X-ray or neutron diffraction which comprises a major peak, usually at values corresponding to a repeat spacing between 4 and 10nm, and sometimes higher order peaks, the first at a Q-value which is  $3^{0.5}$  times the Q- 25 value of the principal peak and the next double the Q-value of the principal peak. M-phases are sometimes referred to in the literature as H-phases.

The viscous isotropic or "VI" phases are typically immobile, non-Newtonian, optically isotropic and are 30 typically transparent, at least when pure. VI phases have a cubic symmetrical diffraction pattern, under X-ray diffraction or neutron scattering, with a principal peak and higher order peaks at  $2^{0.5}$  and  $3^{0.5}$  times the Q-value of the principal peak.

These cubic liquid crystalline phases are sometimes observed immediately following the micellar phase at ambient temperature as the concentration of surfactant is increased. It has been proposed that such VI 35 phases, sometimes referred to as  $I_1$  phase, may arise from the packing of micelles (probably spherical) in a cubic lattice. At ambient temperature a further increase in surfactant concentration usually results in hexagonal phase ( $M_1$ ), which may be followed by a lamellar phase (G).  $I_1$  phases, when they occur, are usually only observed over a narrow range of concentrations, typically just above those at which the  $L_1$ - 40 phase is formed. The location of such VI phases in a phase diagram suggests that the phase is built up of small closed surfactant aggregates in a water continuum.

An inverse form of the  $I_1$  phase (the  $I_2$  phase) has also been reported, possibly between the inverse 45 hexagonal ( $M_2$ ) and  $L_2$  phases. It consists of a surfactant continuum containing a cubic array of water micelles. An alternative form of the VI phase called the  $V_1$  phase has been observed at concentrations between the M and G phases and may comprise a bicontinuous system. This may exhibit an even higher viscosity than the  $I_1$ . An inverse phase, the  $V_2$  phase, between the G and  $M_2$  phases has also been postulated.

A characteristic property of VI phases is commonly observed when a jar or beaker containing such a 50 phase is sharply struck. A distinctive vibration can be felt in the composition. This has given rise to the term "ringing gel" sometimes applied to VI phases and may be in part due to the elasticity of the VI phase. The  $I_1/L_1$  transition temperature will be referred to herein as the melting point of the  $I_1$  phase for convenience, although it is not strictly speaking the melting point since the VI phases are not solids.

All references herein to the formation or existence of specific phases or structures are to be construed, 55 unless the context requires otherwise, as references to their formation or existence at 20°C.

We have now discovered that many of the problems hereinbefore described can be overcome, and the objects of the invention achieved by the use of VI phases. For instance we have discovered that certain VI 55 phases are particularly suitable for use as pre-spotting compositions. They are capable of being cast in a stick or bar form having a high degree of dimensional stability and therefore capable of use in a stick applicator. We have discovered that they are nevertheless easily applied to stained areas of fabric without wetting and with only gentle rubbing. They remain adhering to the fabric as gels at ambient temperature but can be formulated to melt at wash temperatures to form a clear rapidly water soluble liquid or to disperse

readily in wash liquor.

They can incorporate washing enzymes, including mixed enzymes comprising protease and lipase, and also oxidising bleaches, with substantially improved stability. They can also incorporate sensitive ingredients e.g. by adding them to the melt and cooling without spray drying or dry blending.

5 According to a first embodiment, therefore, our invention provides the use of aqueous based surfactant VI phases as cleaning compositions.

According to a second embodiment our invention provides a method of removing soil and/or stains from a surface which comprises applying thereto an aqueous based surfactant VI phase and washing said surface with water.

10 According to a third embodiment our invention provides a method of removing soil and/or stains from laundry which comprises dissolving a surfactant VI phase in water to form a wash liquor and contacting said laundry with said wash liquor.

According to a fourth embodiment our invention provides a composition for use as a cleaning composition, which, at some temperature below 100°C is a clear liquid L<sub>1</sub> phase aqueous based surfactant solution which forms a VI phase on cooling.

15 According to a fifth embodiment our invention provides an aqueous based formulation for use as a cleaning composition comprising surfactants in the form of a VI phase which forms an L<sub>1</sub> phase at a transition temperature between 25 and 80°C.

According to a sixth embodiment our invention provides an aqueous based formulation for use as a 20 cleaning composition comprising a mixture of surfactants present as a VI phase having a mean HLB of from 10 to 15.

According to a seventh embodiment our invention provides a stick applicator containing surfactants in the form of a VI phase.

25 According to an eighth embodiment our invention provides an aqueous based cleaning composition for hard surfaces which comprises surfactants present as a VI phase and which may contain suspended abrasive particles.

According to a ninth embodiment the invention provides aqueous based cleaning compositions for use in washing human skin or hair or animal skin or fur comprising surfactants present in the VI phase.

30 According to tenth embodiment the invention provides an aqueous based cleaning composition comprising surfactants present as a VI phase and containing washing enzymes. We prefer that the enzymes comprise a protease and a lipase and preferably also an amylase.

According to a further embodiment the invention provides an aqueous based cleaning composition comprising surfactants present as a VI phase for use in the removal of soils and/or stains from areas of soft furnishings.

35 According to a further embodiment the invention provides an aqueous based cleaning composition, comprising surfactants present as a VI phase, and incorporating an oxidising bleach dispersed therein. Preferably the bleach is encapsulated for example in a film forming polymer or wax to further inhibit degradation.

According to a further embodiment the invention provides cleaning composition comprising heat - 40 and/or water-sensitive materials encapsulated in surfactants present as a VI phase.

According to a further embodiment our invention provides a cleaning composition comprising non-ionic surfactants present as a VI phase and a cationic fabric conditioner.

According to a further embodiment our invention provides a particulate detergent composition comprising surfactants present as VI phase.

45 According to a further embodiment the invention provides an aqueous based cleaning composition comprising surfactants present as a VI phase, wrapped or coated with or encapsulated within a film or sachet of a water soluble polymer.

According to yet another embodiment the invention provides a composition comprising at least one non-ionic relatively hydrophilic surfactant having an HLB greater than 15 which forms L<sub>1</sub> phase, at least one 50 other surfactant having an HLB less than 10, in a proportion based on said relatively hydrophilic surfactant such that the mean HLB of the surfactant mixture lies between 10 and 15 and sufficient water to provide an L<sub>1</sub> phase.

We particularly prefer that the VI phase for use according to any of the aforesaid embodiments of the Invention, and, especially for use as a pre-spotter or hard surface cleaner, or as a main wash detergent (e.g. 55 in unit dose form) should comprise a cubic array of spherical micelles or L<sub>1</sub> phase. The phase is preferably located on the phase diagram between the L<sub>1</sub> and M<sub>1</sub> phases.

Alternatively, especially when used as an encapsulant for bleach, enzymes or other chemically sensitive ingredients, to protect them against a liquid or powder detergent environment, we prefer that the VI phase

be of the bicontinuous cubic type. For example a VI phase located on the phase diagram between the M<sub>1</sub> and G phases, and sometimes referred to as the V<sub>1</sub> phase, is particularly preferred. V<sub>2</sub> and I<sub>2</sub> phases may also be used in this context.

The surfactants are preferably selected to provide a VI phase over a comparatively broad surfactant concentration range e.g. more than ±2% by weight preferably ±5% or greater, which range typically lies above 15% by weight total surfactant based on the weight of the composition e.g. between 20% and 70% by weight surfactant usually between 25% and 60%.

The surfactants are preferably selected to provide a VI phase which melts above 30°C e.g. above 35°C most preferably above 40°C. Preferably the VI phase melts at a temperature substantially below 100°C e.g. below 90°C more preferably below 80°C most preferably below 70°C, especially below 60°C, typically below 55°C, usually below 50°C.

The surfactant mixture preferably has a mean HLB between 10 and 15 e.g. 11 to 14. The surfactants preferably comprise non-ionic surfactants such as ethoxylated alcohols. It has been found that highly ethoxylated fatty alcohols, e.g. more than 10 EO groups, preferably more than 15 EO groups, especially 18 to 50 EO groups form VI phases particularly readily.

Unfortunately the more highly ethoxylated alcohols have too high an HLB for efficient laundry use. However we have discovered that, by blending the more highly ethoxylated alcohols with low HLB surfactants (e.g. ethoxylated alcohols with less than 10 EO, especially less than 5 EO), a mixture having the desired HLB and forming a VI phase with the correct melting point can be obtained.

One way of developing a suitable composition is to select a hydrophilic (preferably non-ionic) surfactant which is known to form a suitable VI phase (e.g. an I<sub>2</sub> phase) and to blend it with sufficient relatively hydrophobic surfactant to obtain the desired HLB. It may be helpful to construct a phase diagram with the relative proportions of the two components on the horizontal axis and total surfactant concentration on the vertical axis. A VI phase region then is identified in the diagram. A range on the horizontal axis embraces the compositions having the correct HLB (which can be calculated) and the "melting point" of the VI phase is generally proportional to concentration. Thus a range on the vertical axis embraces compositions with the desired "melting point". Combining these ranges gives a box within which to select a VI phase. If the phase diagram fails to indicate a suitable VI phase occurring within the box, the experiment may be repeated, substituting a different surfactant for, e.g. the less hydrophilic surfactant.

Other non-ionic surfactants which may be present include:- alkyl phenol ethoxylates, fatty acid ethoxylates, fatty acid monoalkylolamide ethoxylates, fatty alcohol propoxylates, fatty amine alkoxylates and fatty acid glyceryl ester ethoxylates. Other non-ionic compounds suitable for inclusion in compositions of the present invention include mixed ethylene oxide propylene oxide alkoxylates, low relative molecular mass polyethylene glycols e.g. PEG600 and PEG200, ethylene glycol monoesters, alkanolamides, amine oxides and alkyl polyglycosides, alkyl sugar esters including alkyl sucrose esters and alkyl oligosaccharide ester, alkyl capped polyvinyl alcohol and alkyl capped polyvinyl pyrrolidone.

Compositions of the invention may also comprise anionic surfactants, in addition to or instead of non-ionic surfactants. Such anionic surfactants may for example be chosen from the group of:- C<sub>10</sub>-<sub>20</sub> alkyl ethoxy sulphates (including sodium, potassium, ammonium, magnesium, lithium, triethanolamine, diethanolamine or monoethanolamine salts of such ethoxy sulphates, and a sodium/magnesium mixed salt of such ethoxy sulphates), di-sodium alkyl ethoxy sulphosuccinates. Also phosphate esters including fatty alcohol ethoxy phosphate esters and substituted phenol ethoxylated phosphate esters are suitable for compositions of the present invention.

Preferred are the sodium salts of the anionic ethoxylated surfactants for reasons of cost but potassium salts and mixed sodium/potassium salts may have performance advantages.

Other anionic surfactants that may be present include C<sub>10</sub>-<sub>20</sub> alkyl benzene sulphonates, parafin sulphonates, alkyl sulphates, olefin sulphonates, soaps, fatty acid taurides, isethionates and ester sulphonates, alkyl ether carboxylates and alkyl ether polycarboxylates.

The compositions of the invention may optionally include a cationic surfactant, especially a cationic fabric conditioner such as a ditallowyl dimethylammonium salt, a ditallowyl benzalkonium salt or a ditallowyl imidazolinium or amidoammonium salt.

According to a preferred embodiment the products of this invention comprise in percentages by weight based on the weight of the total surfactant and water from 10 to 65% of one or more ethoxylated surfactants (non-ionic and/or anionic surfactants) and from 30 to 90% by weight of water.

Preferably the non-ionic surfactants include at least one chosen from the group comprising ethoxylated C<sub>8</sub>-C<sub>20</sub> e.g. C<sub>12</sub>-C<sub>18</sub> alcohols having an average of 2-80, preferably 3-60, and most preferably 8 to 50 ethyleneoxy groups per molecule. Other non-ionic surfactants include alkyl (C<sub>8</sub>-C<sub>9</sub>) phenol ethoxylates

having a preferred proportion of ethylene oxide of 2-40 units, also ethoxylated C<sub>8</sub>-C<sub>20</sub> fatty acids having the same preferred proportion of ethylene oxide, and mixed ethoxylated propoxylated analogues of the aforesaid non-ionic surfactants having a ratio of propyleneoxy to ethyleneoxy groups between 0 and 0.5. Other non-ionic surfactants include ethoxylated fatty alkyl mono, and di-ethanolamides, fatty alcohol

5 alkoxylates, fatty amine alkoxylate, substituted phenol ethoxylates and ethylene glycol esters. Polyethylene glycol e.g. with relatively low molecule mass are also suitable.

We prefer that the composition contains a protease, lipase and/or amylase. Especially we prefer that the composition comprises a protease and a lipase. Most preferably the composition comprises a protease, a lipase and an amylase.

10 The composition may contain an oxidising bleach such as sodium perborate, builders such as zeolite and/or an inert abrasive such as talc, calcium carbonate, or silica. Solids may generally be introduced by stirring the particulate solid into a VI phase composition which is heated above its melting point, and cooling the resulting mixture of solid and L<sub>1</sub> phase.

15 Electrolytes tend to disrupt the gel structure, however to the extent that they are compatible, we prefer that the composition contains dissolved builder salts such as citrates, carbonates, phosphates, pyrophosphates, polyphosphates and phosphonates.

The applicator may be provided with means for extruding the contents progressively through the open end. For example the extrusion means may comprise a screw extruder, e.g. one in which the rotation of a base member causes a plunger to move along the axis of the container. Alternatively the plunger may be 20 actuated by sliding means such as nested concentric tubes telescoped by pressure between the top and base or lugs projecting laterally through slots in the container.

An alternative to extrusion means is a container whose sides are adapted to be progressively removed to expose the contents as the latter is consumed. For example the side of the container may comprise a foil which can be peeled back or may be in the form of a wooden tube which can be cut back with a knife or 25 pencil sharpener.

A preferred applicator is described with reference to the drawings of which Fig. 1 is a diagrammatic sectional elevation and Fig. 2 is a sectional plan.

The applicator comprises a tube, (1) usually of substantially circular cross section, open at one end, which end is provided with a removable cap (2). The closed end of the tube comprises a rotatable member 30 (3) provided with an externally screw threaded rod (4) which extends along the axis of the tube. The rod 4 passes through and engages a correspondingly threaded hole in the centre of an extruder plate (5) which fits closely and slidably within the tube 1, initially near its closed end 3. Longitudinal ribs (6, 6') project radially from the inside of the tube 1, and engage corresponding slots in the circumference of the extruder plate 5.

35 The open applicator may be filled with the molten composition which is allowed to set to a VI gel, and capped. In use, the cap 2 is removed and the rotatable base member 3 is rotated, causing the rod 4 to rotate and urge the extruder disc up the tube until the gel is exposed. Rotation of the extruder disc is prevented by the ribs 6, 6'. The exposed gel is rubbed on the surface to be treated. The gel is thixotropic and is sufficiently mobile under the shear caused by gentle rubbing to distribute over the surface to be 40 treated and also to maintain a continuous gel surface at the open end of the applicator, even as the gel "stick" is progressively extruded around the rod 4.

The ribs 6,6' can be extended towards the axis, thereby effectively dividing the applicator into two or (by increasing the number of ribs) more compartments. The compartments may be individually filled e.g. with different formulations with relatively little intermingling. They could thus accommodate separate, 45 mutually incompatible components which would be stabilised by the very low permeability of the gel.

As an alternative to the stick applicator the composition may be wrapped or encapsulated in, or coated with, a water soluble polymer such as polyvinyl alcohol or polyvinyl pyrrolidone, for example, the polymer may be used to provide unit dose sachets, which can be added direct to the washing machine.

Conventional unit dose sachets filled with liquid or powder detergent have been found unsuitable for 50 direct addition to washing machines because the ends of each sachet have to be heat sealed. The sealed portion is relatively insoluble and, in time, accumulated sachet ends may cause blockages in the machine. VI phases can be coated with a polymerisable film which is polymerised in situ to provide a fully soluble capsule. Alternatively a cylindrical skin of polymer may be filled with VI gel and heat sealed at the ends. Unit doses of detergent may then be cut from the resulting detergent "sausage" without using the heat 55 sealed ends.

Alternatively the composition may be in particulate form. Particulate compositions may be prepared, for example by prilling the molten composition to form granular prills, or by casting it to a VI phase and flaking the VI phase, e.g. on a drum flaker, to form flakes, or by extruding the plastic composition at a temperature

between its softening point and the temperature at which it is fully liquid to form e.g. needles.

Alternatively the VI detergent may be cast or plodded into the form of bars or tablets. We particularly prefer compositions in the form of unit doses tablets. Such tablets may be separate e.g. separately wrapped or enclosed in separate compartments of a blister pack, or may be cast as a single block or bar subdivided into separable tablets e.g. by grooves or constrictions of the bar.

The VI phase may additionally have, dispersed therein, solid particles of any detergent ingredients which can be mixed with the VI phase at sufficiently elevated temperatures without dissolving therein. Such particles may include builders such as sodium tripolyphosphate, tetrapotassium pyrophosphate, sodium orthophosphate, zeolite, sodium citrate, sodium or potassium carbonate, sodium silicate, sodium nitrilotriacetate, sodium ethylene diamine tetracetate, phosphonates such as acetodiphosphonates, aminotris (methylenephosphonates), ethylenediamine tetrakis (methylenephosphonates), diethylenetriamine pentakis (methylelenephosphonates), triethylene tetramine hexakis (methylene phosphonate) and higher members of the same series of (n)ethylene (n + 1) amine (n + 2) (methylenephosphonate) salts or glycine bis (methylene phosphonate), inorganic fabric conditioners such as bentonite, abrasive such as talc, silica, aluminosilicates, calcite or chalk or a bleach such as sodium perborate, percarbonate or a peroxy hydrate of a phosphate or condensed phosphate. The dispersed phase could optionally include an inert filler such as sodium sulphate. However we do not prefer to include fillers in the composition of this invention. It is an advantage of the invention that the use of fillers can be avoided. The dispersed phase may constitute up to 60% preferably 1 to 30% e.g. 5 to 20% especially 8 to 15% by volume based on total volume of the dispersion.

In addition to incorporating dispersed solid phases in the continuous solid phase, the particulate compositions of the present invention may be dry blended with other powdery or granular compositions. Such blends constitute a less preferred aspect of the invention. Generally an advantage of the invention is the ability to incorporate water and/or heat sensitive ingredients without the inconvenience and inconsistency of dry blending.

Compositions of the invention preferably contain soil suspending agents such as sodium carboxymethyl cellulose typically in proportions of from 0.01 to 3% by weight based on the weight of the composition, especially 0.1 to 2%, e.g. 0.2 to 1%.

The composition preferably contain optical brighteners, which are fluorescent dyes, in proportions of from 0.01 to 3% by weight based on the weight of the composition, preferably 0.1 to 2%, e.g. 0.2 to 1%.

The compositions typically contain fragrances, dyes, pigments and/or preservatives in a total proportion of from 0.1 to 5% by weight, e.g. 0.5 to 3% by weight based on the total weight of the composition.

The compositions of the invention may also comprise conventional amounts of bleach activators such as tetracetoethylenediamine, where an oxidising bleach has been included, foam control agents such as silicone antifoams and/or mineral oils where the compositions are intended for use in front loading washing machines, or foam boosters where the products are intended for use in top loading washing machine or for hand washing.

The invention is illustrated by the following examples in Table 1 and Table 2 in which all proportions are expressed as percentage by weight based on the total weight of the composition:

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Table 1

	Examples of compositions of the invention.					
	1	2	3	4	5	6
C <sub>12</sub> -C <sub>18</sub> alcohol ethoxylate (3EO)	5.6	-	8.0	4.4	8.75	7.2
C <sub>12</sub> -C <sub>18</sub> alcohol ethoxylate (8EO)	-	13.3	-	3.5	-	-
C <sub>12</sub> -C <sub>14</sub> alcohol ethoxylate (12EO)	-	-	-	14.0	-	-
C <sub>16</sub> -C <sub>18</sub> alcohol ethoxylate (20EO)	-	6.7	10.0	-	10.0	25.3
C <sub>16</sub> -C <sub>18</sub> alcohol ethoxylate (50EO)	19.4	20.0	12.0	13.1	11.25	-
Perfume/dyes etc.	1.0	1.0	1.0	1.0	1.0	1.0
Enzyme Solution	1.0	1.0	1.0	1.0	1.0	1.0
Water	Balance	Balance	Balance	Balance	Balance	Balance
Melting point °C	40	50	40	45	55	45
% surfactant concentration (Based on total weight of composition)	25	40	30	35	30	32.5

Table 2

	Examples of compositions of the invention.					
	7	8	9	10	11	12
5	C <sub>12</sub> -C <sub>18</sub> alcohol ethoxylate (8EO)	20.0	8.9	12.5	10.7	6.7
	C <sub>12</sub> -C <sub>14</sub> alcohol ethoxylate (12EO)	-	31.1	15.5	16.0	-
10	C <sub>16</sub> -C <sub>18</sub> alcohol ethoxylate (15EO)	-	-	-	13.3	13.3
	C <sub>16</sub> -C <sub>18</sub> alcohol ethoxylate (20EO)	20.0	-	12.0	-	20.0
	Perfume/dyes etc.	1.0	1.0	1.0	1.0	1.0
	Enzyme solution	1.0	1.0	1.0	1.0	1.0
	Water	Balance	Balance	Balance	Balance	Balance
	melting point °C (approximate)	40	30	35	45	50
15	% surfactant concentration (Based on total weight of composition)	40	40	40	40	50

The enzymatic solution used in examples 1 to 12 comprises a mixture of protease, amylase and lipase provided by a 1:1:2 mixture by weight of the proprietary solutions 'SAVINASE 16.0 LDX', 'TERMAMYL 300.0 LDX' and 'LIPOLASE 100L' respectively. 'SAVINASE', 'TERMAMYL' and 'LIPOLASE' are registered trademarks of NOVO NORDISK A/S.

The compositions formed clear VI gels which melted over a range of approximately +2°C of the melting points given above. The gels were heated above their melting points and poured into screw applicators, as described with reference to the drawings, and cooled.

The compositions of the examples 1 to 12 were developed by constructing a phase diagram and selecting from within the I<sub>1</sub> phase area, compositions having the desired HLB value and "melting point".

Areas of I<sub>1</sub> were found to be present in many of the diagrams. Figure 3 is a generalised phase diagram (not to scale) indicating the relationship of the M<sub>1</sub>, I<sub>1</sub> and L<sub>1</sub> phases for typical compositions of the invention comprising water and two surfactants: a higher HLB value non-ionic surfactant, A, and a lower HLB surfactant, B. A number of compositions were found to exhibit I<sub>1</sub> phases which extend into the useful laundry HLB range (e.g. 11 to 15).

To identify a composition suitable for use as a pre-spotting gel an HLB value of 11 to 15 and a melting point of approximately 40°C are preferred. Selecting compositions from wide areas of I<sub>1</sub> phase with similar 'melting point' temperatures on the phase diagrams provides formulations which are able to withstand variations in manufacture.

The gels were easily extruded and were compared with a variety of commercially available pre-spotting preparations on artificially stained test cloths. In each case the composition of the invention was more easily applied than the commercial preparation, and was more economical in terms of the amount applied. The compositions gave substantially improved stain removal after washing under defined conditions in a standardised washing machine at 60°C, (200ppm CaCO<sub>3</sub> water hardness) when compared to stain removal achieved on test clothes which did not receive treatment with the pre-spotting composition. The degree of whiteness of the fabric after treatment is determined by reflectance measurement.

The improvement in stain removal achieved by the use of compositions according to the invention is illustrated below in Table 3:

#### 45 Method of evaluation of pre-spotting performance

1. Two 3 inch square pieces of each standard pre-stained cloth (below) were completely treated on both sides using the pre-spotting composition, example 7 (table 2) in a stick applicator.
- 50 2. All the test cloths were then immediately washed together at 60°C in a standardised automatic washing machine, with 100mls (7.4grams per litre of wash water) of a commercial concentrated laundry liquid, and using calcium carbonate to dose the washing water to achieve a water hardness of 200 parts per million of calcium carbonate. The test clothes were rinsed in hardness adjusted water.
- 55 3. After air drying and ironing two light reflectance readings were taken on each side of every cloth, using a Minolta light reflectance meter model CR200. The eight light reflectance readings thus obtained were averaged and converted to percentage soil or stain removal by the formula below:

$$\% \text{ removal} = \frac{W_1 - W_2}{W_1} \times 100$$

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where:

$W_1$  is the reflectance reading of the laundered fabric.

$W_2$  is the reflectance reading of soiled/stained fabric.

10  $W$  is the reflectance reading of unsoiled fabric of the correct type.

Cloths 101, 104, 112, 114, 116 and 117 are supplied by the 'Swiss Federal Laboratories for materials testing and research - Switzerland' and cloths 10C, 20C, 10D, 20D, 30D are supplied by Washereiforfehung Krefeld (WFK) - Germany. All of the aforementioned cloths used for evaluation of the pre-spotter are recognised as standard test cloths in the detergent industry. Tea, coffee and blackcurrant juice test cloths were prepared in-house, by manual staining of cloth. The test fabrics are measured for reflectance values before and after laundering.

Table 3

Evaluation of a composition according to the invention as a pre-spotting formulation for laundry.			
		Prespotted and washed Cloths	Washed only Cloths
CLOTH NO.	SOIL	% SOIL REMOVAL	% SOIL REMOVAL
101	Carbon/Olive oil	21.4	16.1
104	Carbon/Olive oil	24.0	25.9
10C	Carbon/Wool grease	42.4	47.0
20C	Carbon/Wool grease	25.9	24.7
10D	Pigment/sebum	66.2	60.5
20D	Pigment/sebum	72.2	57.5
30D	Pigment/sebum	43.1	32.8
		mean 42.2	mean 37.8
CLOTH NO.	STAIN	% STAIN REMOVAL	% SOIL REMOVAL
112	Cocoa	53.0	44.7
114	Red wine	53.1	45.4
116	Blood/milk/carbon	50.1	47.2
117	Blood/milk/carbon	66.9	64.9
TEA	-	40.7	39.2
COFFEE	-	23.3	19.6
BLACKCURRANT	-	42.7	41.7
		mean 47.1	mean 43.2

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All cloths are cotton except for 104 and 20C (65/35 polyester cotton), 20D (polycotton) and 30D (polyester).

The improvement in washing performance as ascertained by the removal of soils and stains from standard test cloths, is shown by a 12% increase in the soil removal result effected by the use of the aforementioned pre-spotting composition, based on the soil removal achieved by use of a washing liquid detergent only.

Similarly, a 9% increase in stain removal on standard test cloths is achieved by the use of the pre-spotting composition based on the result achieved by normal washing of the test cloths only.

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## Claims

1. The use of aqueous based surfactant VI phases as cleaning compositions.

2. A method for the use according to claim 1 of aqueous based surfactant VI phases to remove soils and/or stains from a surface which comprises applying to the surface the aqueous based surfactant VI phase and washing said surface with water.
- 5 3. A method for the use according to claim 1 of aqueous based surfactant VI phases to facilitate the removal of soils and/or stains from laundry by applying to the surface of the laundry the aqueous based surfactant VI phase prior to washing said laundry in an aqueous wash liquor.
- 10 4. A method for the use according to claim 1 of an aqueous based surfactant VI phase to remove soils and stains from the fibres or fabric of soft furnishings which comprises applying to the surface of the soft furnishings the aqueous based surfactant VI phase and washing with water.
- 15 5. A method for the use according to claim 1 of aqueous based surfactant VI phases to remove soils and/or stains from laundry which comprises dissolving the surfactant VI phase in water to produce a wash liquor and contacting the laundry with the wash liquor.
- 20 6. A composition for use according to claim 1 as a cleaning composition which at some temperature below 100°C exists as a clear liquid L<sub>1</sub> phase aqueous based surfactant solution and which forms a VI phase on cooling.
7. An aqueous based formulation for use according to claim 1 as a cleaning composition comprising surfactants in the form of a VI phase which forms an L<sub>1</sub> phase at a transition temperature between 35°C-80°C.
- 25 8. An aqueous based formulation for use according to claim 1 as a cleaning composition comprising a single surfactant system or a mixture of surfactants present as a VI phase having an HLB value, or a mean HLB value respectively of 10-15.
9. A composition comprising at least 1 non-ionic relatively hydrophilic surfactant having an HLB of 15 or 30 greater which forms an L<sub>1</sub> phase and at least 1 other surfactant having an HLB value of 10 or less, in a proportion based on the relatively hydrophilic surfactant such that the mean HLB of the surfactant mixture lies between 10 and 15, and sufficient water to provide an L<sub>1</sub> phase.
- 35 10. A method according to either of claims 2 and 3 of applying an aqueous based formulation comprising surfactants in a VI phase to a surface to remove soils and/or stains by means of a stick applicator.
11. A stick applicator containing surfactants in the form of a VI phase.
- 40 12. An aqueous based cleaning composition for use according to claim 1 to clean hard surfaces which comprises surfactant present as a VI phase which contains suspended abrasive particles.
13. An aqueous based cleaning composition for use according to claim 1 in washing human skin or hair or animal skin or fur comprising surfactants present as a VI phase.
- 45 14. An aqueous based surfactant composition comprising surfactants present as a VI phase and containing washing enzymes.
15. A composition according to claim 14 wherein said enzymes comprise a protease, amylase and/or lipase.
- 50 16. An aqueous based cleaning composition comprising surfactants present as a VI phase and incorporating an oxidising bleach dispersed therein.
17. An aqueous based cleaning composition comprising surfactants present as a VI phase, wrapped or 55 coated with or encapsulated within a film or sachet of a water soluble polymer.
18. A composition according to any of claims 6 to 9 or 12 to 17 comprising a cubic array of spherical micelles or an L<sub>1</sub> phase.

19. An aqueous based cleaning composition comprising highly water sensitive materials encapsulated in surfactants present as a bicontinuous cubic VI phase, or I<sub>2</sub> phase.
20. A method of making a particulate composition for use according to claim 1 which comprises heating a surfactant composition which forms a VI phase above its softening point and mixing it with builder, bleach, enzyme, fabric conditioner and/or detergent ancillary ingredients and cooling the mixture.  
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21. A method according to claim 20 wherein said composition is heated until it is liquid and spray cooled.
- 10 22. A method according to claim 20 wherein said composition is heated until it is plastic and extruded prior to cooling.

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Fig. 1

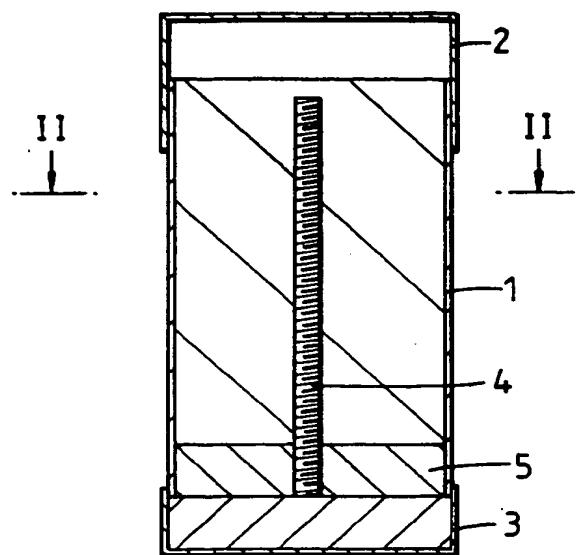


Fig. 2

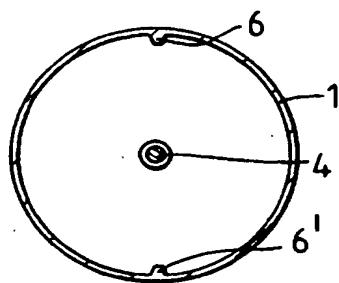


Fig. 3

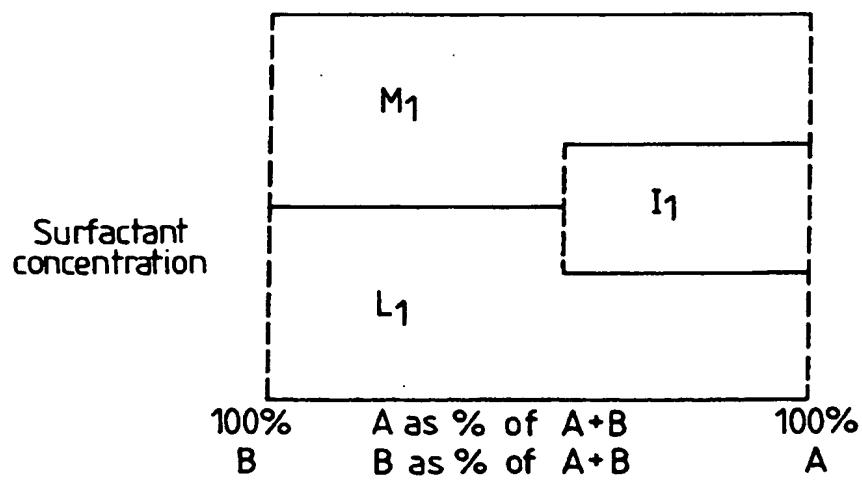


Fig. 1

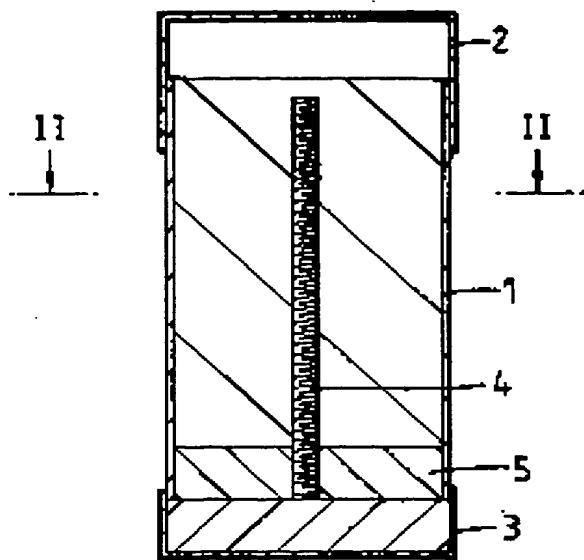


Fig. 2

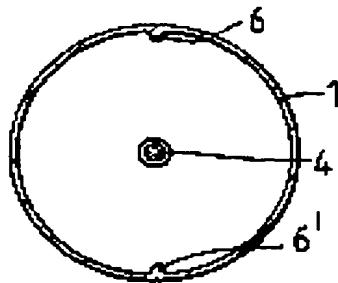
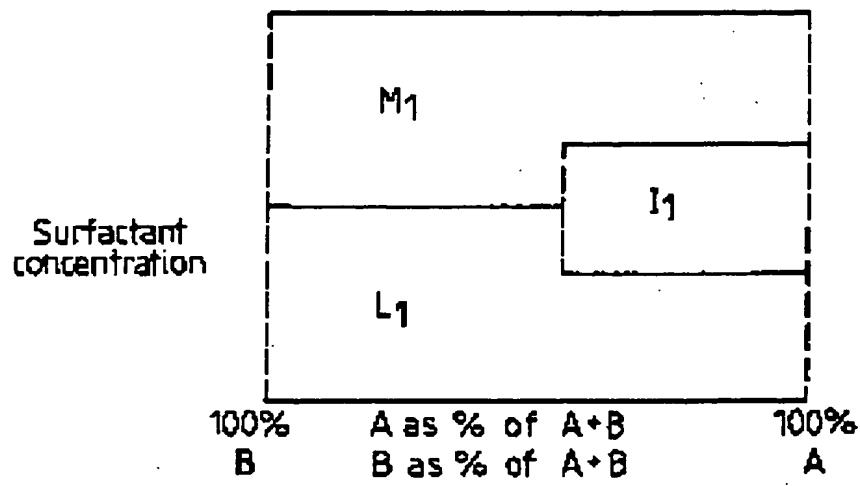


Fig. 3



(19)



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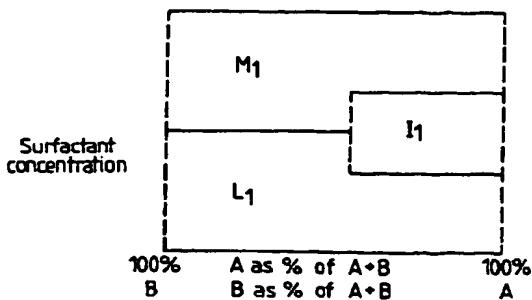
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### (54) Novel cleaning compositions

(57) Aqueous based VI phases (ringing gels) are used as laundry pre-spotters, e.g. in stick applicators, and for a variety of cleaning applications. The compositions typically comprise a non-ionic surfactant having an HLB greater than 15, a surfactant having an HLB below 10 and water.

Fig. 3



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## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 8271

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
P, X	EP-A-0 530 708 (ALBRIGHT & WILSON LTD.) 10 March 1993 * page 1 - page 7 * * page 12; claims * ---	1-5, 12-16,18	C11D17/00
X	US-A-4 026 818 (CIAUDELLI JOSEPH P.) 31 May 1977 * column 1, line 5 - line 28; claims * ---	1,13	
X	DE-A-41 08 548 (MÜLLER B.) 25 July 1991 * the whole document * ---	1,13	
X	US-A-4 465 663 (SCHMOLKA IRVING R.) 14 August 1984 * column 1, line 5 - column 2, line 27; claims * ---	1,13	
X	EP-A-0 077 674 (UNILEVER PLC.) 27 April 1983 * page 4 - page 5; claims * ---	1	
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A	EP-A-0 414 549 (ALBRIGHT & WILSON LTD.) 27 February 1991 * claims; example 2 * ---	1,12	
		-/-	
The present search report has been drawn up for all claims			
Place of search  THE HAGUE	Date of completion of the search  13 November 1995	Examiner  Serbetsooglou, A	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



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Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 8271

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CLS)						
A	EP-A-0 288 858 (HENKEL KGAA.) 2 November 1988 * the whole document * ---	1,3							
A	EP-A-0 100 125 (THE PROCTER & GAMBLE CO.) 8 February 1984 * page 6 - page 15; claims 1,8-10 * ---	1,2, 14-16							
A	EP-A-0 081 908 (UNILEVER PLC.) 22 June 1983 * page 6; claims 1-4 * ---	1,2, 14-16							
A	EP-A-0 043 327 (L' OREAL) 6 January 1982 * claims * -----	1							
TECHNICAL FIELDS SEARCHED (Int.Cl.5)									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>13 November 1995</td> <td>Serbetoglou, A</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	13 November 1995	Serbetoglou, A
Place of search	Date of completion of the search	Examiner							
THE HAGUE	13 November 1995	Serbetoglou, A							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
<small>           X : particularly relevant if taken alone            Y : particularly relevant if combined with another            document of the same category            A : technological background            O : non-written disclosure            P : intermediate document         </small>									